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TITLE: Nanostructured moulded bodies and layers and method for producing same

Abstract Text (4):

b2) application of said composition of step a) onto a substrate; and

Brief Summary Text (7):

2) application of the composition of step a) onto a substrate;

Brief Summary Text (10):

Alternatively or in addition thereto, a (further) thermal densification of said moulded article or said layer, respectively, at a temperature of at least 250.degree. C., preferably at least 400.degree. C. and particularly at least 500.degree. C., may be effected. In the case of a layer on a substrate thermal densification may naturally only be carried out if the substrate material can resist such high temperatures without impairment, as this is the case with, e.g., glass and many metals and metal alloys, respectively (but also with some plastics).

Brief Summary Text (14):

The solid nanoscaled inorganic particles may consist of any material but preferably they consist of metals and particularly of metal compounds such as (optionally hydrated) oxides, such as ZnO, CdO, SiO₂, TiO₂, ZrO₂, CeO₂, SnO₂, Al₂O₃, In₂O₃, La₂O₃, Fe₂O₃, Cu₂O, Ta₂O₅, Nb₂O₅, V₂O₅, MoO₃ or WO₃; chalcogenides such as sulfides (e.g. CdS, ZnS, PbS and Ag₂S), selenides (e.g. GaSe, CdSe and ZnSe) and tellurides (e.g. ZnTe or CdTe), halides such as AgCl, AgBr, AgI, CuCl, CuBr, CdI₂ and PbI₂; carbides such as CdC₂ or SiC; arsenides such as AlAs, GaAs and GeAs; antimonides such as InSb; nitrides such as BN, AlN, Si₃N₄ and Ti₃N₄; phosphides such as GaP, InP, Zn₃P₂ and Cd₃P₂; phosphates, silicates, zirconates, aluminates, stannates and the corresponding mixed oxides (e.g. those having a perovskite structure such as BaTiO₃ and PbTiO₃).

Brief Summary Text (15):

Preferably, the solid nanoscaled inorganic particles employed in step a) of the process according to the present invention are those of oxides, sulfides, selenides and tellurides of metals and mixtures thereof. Particularly preferred according to the present invention are nanoscaled particles of SiO₂, TiO₂, ZrO₂, ZnO, Ta₂O₅, SnO₂ and Al₂O₃ (in any modification, particularly in the form of boehmite, AlO(OH)) as well as mixtures thereof.

Brief Summary Text (17):

The production of the nanoscaled solid particles employed according to the present invention may be effected in usual manner, e.g., by flame pyrolysis, plasma processes, condensation processes in the gas phase, colloid techniques, precipitation processes, sol-gel processes, controlled nucleation and growth processes, MOCVD processes and (micro) emulsion processes. Said processes are described in detail in the literature. Particularly, metals (for example following the reduction of the precipitation processes), ceramic oxide systems (by precipitation from solution) but also salt-like or multicomponent systems may, for example, be used. The salt-like or multicomponent systems also encompass semiconductor systems.

Brief Summary Text (41):

In step b) of the process according to the present invention said free-flowing composition of step a) is either introduced into a suitable mould in order to produce a moulded article, or is applied onto a desired substrate in order to coat said substrate completely or partially. The coating methods suitable for said purpose are the common

"ones known to the skilled person. Examples thereof are dip coating, spray coating, doctor blade coating, painting, brushing, spin coating, etc.

Brief Summary Text (42):

Prior to introduction into the mould or application onto a substrate, said free-flowing composition may be adjusted to a suitable viscosity, for example by adding solvent or evaporating volatile components (particularly solvent already present).

Brief Summary Text (43):

Substrates made of any material, particularly of plastics, metals and glass, are suitable for being coated with the free-flowing composition of step a) of the process according to the present invention. Prior to the application of said free-flowing composition said substrate materials may optionally be subjected to a surface treatment (e.g. degreasing, roughening, corona discharge, treatment with a primer, etc.). Especially when substrates made of plastics are coated a suitable adhesion may be provided by adding a suitable monomeric polymerizable compound and/or according to the preferred embodiment described in more detail below.

Brief Summary Text (44):

Among the metal substrates which may be coated according to the present invention metals such as aluminum, copper, zinc, nickel and chromium, and metal alloys such as (stainless) steel, brass and bronze may be mentioned as examples. Examples for suitable substrates made of plastics are those made of polycarbonate, polyesters, polyamides, polystyrene, poly(meth)acrylates (e.g. polymethylmethacrylate), PVC, polyolefins (such as polyethylene and polypropylene), rubbers (ABS, NBS, etc.) and polyphenylenesulfide, to name but the most important ones.

Brief Summary Text (45):

In step c) of the process according to the present invention a polymerization and/or polycondensation of the polymerizable/polycondensable surface groups of said solid nanoscaled inorganic particles (and, optionally, of the polymerizable/polycondensable groups of the monomeric or oligomeric species additionally employed) is carried out. Said polymerization/polycondensation may be carried out in a manner known to the person skilled in the art. Examples of suitable processes are thermal, photochemical (e.g. by means of UV radiation), electron beam curing, laser curing, room temperature curing, etc. Such a polymerization/poly-condensation is optionally effected in the presence of a suitable catalyst or starter (initiator), respectively, which is added to said free-flowing composition of step a) at the latest immediately before the introduction thereof into the mould or the application thereof onto the substrate, respectively.

Brief Summary Text (52):

Said polymerization/polycondensation may be preceded by a removal of further volatile, non-polymerizable/non-polycondensable compounds from the composition present in the mould or on the substrate, respectively. Said removal of volatile components may, however, be effected also or additionally, respectively, at the polymerization/polycondensation stage or thereafter.

Brief Summary Text (55):

The production of a layer may, for example, be carried out by adding to sols featuring, for example, oxidic or sulfidic nanoparticles hydrolyzable silanes having polymerizable/polycondensable groups at a concentration of preferably not more than 100%, particularly not more than 75% by weight (based on said nano-particles). Following the adjustment of the viscosity by addition or removal, respectively, of solvent (e.g. alcohol) and after the addition of a photoinitiator (e.g. at a concentration of 5% by weight based on the silane employed) a curing of the layer on the selected substrate with preferably UV light results in transparent, crack-free and homogeneous layers. A thermal post-treatment at, for example, 60 to 100.degree. C. usually results in a significant improvement in the layer properties; said post-treatment is, however, not indispensable. The layers thus produced have good abrasion resistance. Since in said process the thermal post-treatment may be carried out at relatively low temperatures, substrates having low thermal stability may also be used without any problems. As already mentioned above, the adhesion of the layer to the substrate may be adjusted by varying the amount and type of silane employed and by adding an additional organic monomer (methacrylate, acrylate, etc.) at low concentrations (for example, <5% by wt.), thereby, for example, both glass and plastics may be coated. The co-use of the fluorinated silanes mentioned above in the surface modification furthermore results in easy-to-clean layers on the corresponding substrates and in a reduction of the surface energy, respectively, while the addition of, e.g., surfactants can increase the surface energy.

Brief Summary Text (56):

According to a preferred embodiment of the present invention, especially for the coating of substrates made of plastics, nanoparticles (particularly those of AlOOH, ZrO₂, TiO₂ and the like) are dispersed at relatively high concentrations (usually at least 15% and preferably at least 20% by wt. or at least 7% or 10%, respectively, by volume, preferred upper limits being 80% by wt., particularly 60% by wt. or 40% by volume, particularly 25% by volume, respectively) in a liquid system comprising as essential component at least one hydrolyzable silane featuring a polymerizable/polycondensable group (e.g. one of the above general formula (I)) and subsequently a (conventional) prehydrolysis of said silane is carried out. In addition to said silane featuring a polymerizable/polycondensable group other hydrolyzable components may optionally be present, particularly other (optionally fluorinated) silanes (e.g. those of the above general formula (II)) and/or hydrolyzable compounds (e.g. alkoxides, halides) of metals of the main and sub-groups of the Periodic Table (e.g. Al, Ti, Zr). After the prehydrolysis, further species having more than one (preferably two) copolymerizable/copolycondensable groups (in particular those of the above general formula (III), preferably in amounts of up to 40%, particularly up to 30% and particularly preferred up to 15% by wt.) may be added. As polymerizable groups (meth)acrylate groups are particularly preferred. Prior to the application onto a plastic substrate a solvent (e.g. an alcohol) may be added to said system in order to adjust the viscosity thereof, as well as conventional paint additives (see below). Although the resulting coating composition may be cured thermally (preferably following the addition of a corresponding thermostarter) it has surprisingly been found that when using a photoinitiator (preferably in the conventional amounts given above) even a (sole) photochemical curing (preferably by UV light) results in a highly scratch-resistant, transparent layer which, moreover, shows good adhesion to most plastics substrates without pretreatment of the surfaces thereof (e.g. in the case of polycarbonates, polystyrene, poly(meth)acrylate, etc.).

Brief Summary Text (57):

Of course, dyes, pigments, matting agents, etc. may be added to the corresponding coating composition if a colored or non-transparent, respectively, layer is desired. Examples of further conventional additives for compositions of the described type are flow additives, UV absorbers, antioxidants (e.g. HALS), antistatic agents, surfactants (for hydrophilic surfaces) and fluorinated compounds (for hydrophobic/oleophobic surfaces).

Brief Summary Text (59):

The moulded articles available according to the present invention are suitable for a number of applications. Only by way of example, the following fields of application may be mentioned in the present context: rapid prototyping, e.g. in the medical field (for prostheses, simulation of organs), prototyping in the field of automobiles (design models, motor components, etc.), optical elements, development of dies, development of testing procedures.

Brief Summary Text (60):

In the case of the layers according to the present invention scratch-resistant coatings having functional properties (anti-reflex, protection against corrosion, hydrophilic properties, hydrophobic properties, antistatic layers) may be mentioned. Coatable materials include those made of transparent and non-transparent plastics, glass, metals, stone, wood, paper and textiles but are not limited thereto.

Brief Summary Text (61):

The above coating compositions are particularly suitable for the coating of constructions and parts thereof; means of locomotion and of transport and parts thereof; operating equipment, devices and machines for commercial and industrial purposes and research, and parts thereof; domestic articles and household equipment and parts thereof; equipment, apparatus and accessories for games, sport and leisure, and parts thereof; and also instruments, accessories and devices for medical purposes and the sick. Said compositions are also highly suitable for the provision of interference layers. Specific examples of coatable materials and articles are indicated below.

Brief Summary Text (63):

Interior and exterior facings of buildings, floors and staircases made of natural stone, concrete, etc., floor coverings of plastic, fitted and loose carpets, base boards (skirting boards), windows (especially window frames, window sills, glazing of glass or plastic and window handles), Venetian blinds, roller blinds, doors, door handles, WC, bath and kitchen fittings, shower cabinets, sanitary modules, lavatories,

· pipes, radiators, mirrors, light switches, wall and floor tiles, lighting, letter boxes, roof tiles, guttering, aerials, satellite dishes, handrails of balconies and moving stairways, architectural glazing, solar collectors, winter gardens, walls of lifts; memorials, sculptures and, generally, works of art made of natural stone (e.g. granite, marble), metal, etc., especially those erected outdoors.

Brief Summary Text (67):

Moulds (e.g. casting moulds, especially those made of metal), hoppers, filling units, extruders, water wheels, rollers, conveyor belts, printing presses, screen-printing stencils, dispensing machines, (machine) housings, injection-moulded components, drill bits, turbines, pipes (interior and exterior), pumps, sawblades, screens (for example for scales), keyboards, switches, knobs, ball bearings, shafts, screws, displays, solar cells, solar units, tools, tool handles, containers for liquids, insulators, capillary tubes, lenses, laboratory equipment (e.g. chromatography columns and hoods) and computers (especially casings and monitor screens).

Brief Summary Text (73):

Prostheses (especially for the limbs), implants, catheters, anal prostheses, dental braces, false teeth, spectacles (lenses and frames), medical instruments (for operations and dental treatment), plaster casts, clinical thermometers and wheel-chairs, and also, quite generally, hospital equipment.

Brief Summary Text (74):

In addition to the above articles it is also possible, of course, to coat other articles and parts thereof, advantageously, with the above coating compositions, examples being jewellery, coins, works of art (for example paintings), book covers, gravestones, urns, signs (for example traffic signs), neon signs, traffic light pillars, CDs, wet-weather clothing, textiles, postboxes, telephone booths, shelters for public transport, protective goggles, protective helmets, films (for example for packaging foods), telephones, seals for water taps, and quite generally all articles produced from rubber, bottles, light-, heat- or pressure-sensitive recording materials (before or after recording, for example photos), and church windows.

Brief Summary Text (76):

Optical filters: anti-reflex and reflex filters in the field of glasses, displays, screens, semiconductor lasers, microlens coatings, solar cells, "damage-resistant" laser layers.

Brief Summary Text (80):

Bakable layers: color filters on metals, interference filters on glass such as, e.g., band pass filters, anti-reflex filters, absorption filters and beam splitting devices.

Detailed Description Text (21):

To the sol of Example 3, 0.08 g of Cyacure.RTM. UVI-6974 (Ciba-Geigy) and 0.02 g of 1-methylimidazole are added. After intensive stirring the mixture is filtered and can then be employed as coating composition. Glass plates (10 cm.times.10 cm.times.2 mm) are cleaned with 2-propanol and dried in air prior to the coating operation.

Detailed Description Text (22):

The coating composition is applied onto the substrate in a defined manner by spin coating. The layer thickness is controlled by the rotational speed of the substrate.

Detailed Description Text (23):

A combined UV/IR dryer (Beltron Company) is used for curing the layer. The apparatus used features two mercury lamps for irradiation with UV light, a IR radiation device the output whereof can be used to control the surface temperature, and a conveyor belt on which the substrates can be passed under said UV/IR irradiation device with defined speed. The output of the mercury lamps is 400 mW/cm.sup.2 each.

Detailed Description Text (24):

The IR irradiation device is adjusted to 120.degree. C., the speed of the conveyor belt is 2.6 m/min, and the coated substrates are passed under at these setpoints for a total of three times.

Detailed Description Text (28):

Using the coating material of Example 3, polycarbonate plates (10 cm.times.10 cm.times.2 mm; pretreatment as described in Example 6) are coated and cured according to the process of Example 6. Differences: the IR irradiation device is set at 100.degree. C., and the last curing step is a thermal post-treatment at 100.degree. C.

· in a circulating air drying cabinet for 30 minutes.

Detailed Description Text (31) :

Using the coating material of Example 3, polymethylmethacrylate plates (10 cm.times.10 cm.times.2 mm; pretreatment as described in Example 6) are coated and cured according to the process of Example 6. Differences: no IR irradiation, and the last curing step is a thermal post-treatment at 80.degree. C. in a circulation air drying cabinet for 60 minutes.

Detailed Description Text (34) :

To the coating material of Example 4 there are added 0.72 g of CyraCure.RTM. UVI-6974, 0.36 g of 1-methylimidazole and 10 g of a 0.02 percent by weight solution of aluminum tributoxyethanolate in 2-isopropoxyethanol and thoroughly mixed therewith. The necessary dilution is effected by adding 50 g of 2-isopropoxyethanol. Using said coating material, polycarbonate plates (see Example 7) are coated and cured according to the process of Example 7. Differences: the substrates are passed under four times at a speed of the conveyor belt of 2 m/min, and the last curing step is a thermal post-treatment at 100.degree. C. in a circulating air drying cabinet for 60 minutes.

Detailed Description Text (40) :

The coating material according to Example 5 is provided with initiators according to Example 8 and cured according to the process described in Example 8.

Detailed Description Text (44) :

Transmission (500 nm): Spectroscopic (coating the substrates on one side)

Detailed Description Text (45) :

Reflection (550 nm): Spectroscopic (backside of substrates uncoated and blackened)

Detailed Description Text (46) :

Adhesion (layer on substrate): Cross-cut adhesion test and tape test according to DIN 53151 and DIN 58196

Detailed Description Text (49) :

Coating of Substrates Made of Plastic

Detailed Description Text (50) :

248.8 g (1 mole) of MPTS there are added with stirring 136.84 g (43% by weight based on the total solids content) of AlOOH nanopowder (Sol P3, 15 nm, Degussa). Hydrolysis is effected by slowly adding thereto 36 g (2 moles) of deionized water and 2.5 hrs of refluxing at 100.degree. C. The cooled prehydrolysate is diluted to a solids content of 45% with 282 g of 1-butanol, and 3.5 g (0.5% by wt.) of Byk.RTM.-306 are added thereto as leveling agent. For UV polymerization, 5.46 g (3% by moles based on the double bonds present) of benzophenone are added as photostarter. The application of the coating system onto various plastic materials is effected by spin coating. The curing of the layer is achieved by UV irradiation for 2 minutes by mercury lamp.

Detailed Description Text (51) :

The coating shows good adhesion (CC/TT=0/0) without pretreatment of the substrate e.g. on PMMA. After 1000 cycles (Taber-Abraser, CS-10F, 500 g/roll) the scratch-resistant coating shows an abrasion hardness of 11%.

Detailed Description Text (53) :

Coating of Substrates Made of Plastic

Detailed Description Text (55) :

The coating shows good adhesion (CC/TT=0/0) without pretreating the substrate, e.g. on PMMA. After 1000 cycles (Taber-Abraser, CS-10F, 500 g/roll) the scratch-resistant coating has an abrasion hardness of 9%.

Detailed Description Text (57) :

Coating of Substrates Made of Plastic

Detailed Description Text (58) :

To 248.8 g (1 mole) of MPTS there are added with stirring 99.52 g (31% by wt. based on the total solids content) of AlOOH nanopowder (Sol P3, 15 nm, Degussa). Hydrolysis is effected by slowly adding thereto 36 g (2 moles) of deionized water and 2.5 hrs of refluxing at 100.degree. C. To the cooled prehydrolysate there are added 49.5 g (15% by moles) of TEGDMA and 3.9 g (0.5% by wt.) of Byk.RTM.-306 as leveling agent, and the

• mixture is diluted to a solids content of 45% with 343 g of 1-butanol. For UV polymerization, 0.6 g (2.5% by moles based on the double bonds present) of benzophenone are added as photostarter. The application of the coating system onto various plastic materials is effected by spin coating. The curing of the layer is carried out by UV irradiation for 2 minutes by means of a mercury lamp.

Detailed Description Text (59):

The coating shows good adhesion (CC/TT=0/0) without pretreatment of the substrate, e.g. on PMMA. After 1000 cycles (Taber-Abraser, CS-10F, 500 g/roll) the scratch-resistant coating has an abrasion hardness of 15%. The dimethacrylate results in an increase in the flexibility and the water stability of the coating. (Maintenance at 65.degree. C. in deionized water>14 days, without dimethacrylate 7 days).

Detailed Description Paragraph Table (1):

	Refractive Index	Substrate	Transmission	Reflection	No.	Material	(550 nm)	[%]										
[%]	Adhesion	6 Glas	1.91	78.5	20	0/0	7 PC	1.91	81	19	0/0	8 PMMA	1.91	78.5	20	0/0	9 PC	
1.47	91	8 0/0	10	PMMA	1.47	91	8 0/0	11	PC	1.44	95	2.5	0/0					

CLAIMS:

1. A process for producing a nanostructured moulded article or layer, comprising the following steps:

- (a) providing a free-flowing composition containing solid nanoscale inorganic particles having polymerizable and/or polycondensable organic surface groups thereon;
- (b1) introducing the composition of step (a) into a mould; or
- (b2) applying the composition of step (a) onto a substrate; and
- (c) polymerizing and/or polycondensing the surface groups of the solid particles, thereby forming a nanostructured moulded article or layer.

7. A process of claim 1 where the solid nanoscale inorganic particles are particles of metal compounds.

8. A process of claim 7 where the solid nanoscale inorganic particles are particles of the oxides, sulfides, selenides, and tellurides of metals, and mixtures thereof.

18. A process of claim 1 where the substrate of step (b2) is a plastic, metal, or glass substrate.

20. A process for producing a nanostructured layer on a plastic substrate, comprising the following steps:

- (a) providing a dispersion of nanoscale metal oxide particles in a system comprising at least one hydrolyzable silane containing at least one polymerizable and/or polycondensable group at a concentration of at least 15% by wt., and subsequently prehydrolyzing the at least one hydrolyzable silane;
- (b) applying the composition of step (a) to a plastic substrate to form a layer; and
- (c) photochemically curing the layer of step (b).

21. A process of claim 20 where the nanoscale metal oxide particles are particles of Al._{sub.2} O._{sub.3}, TiO._{sub.2} and/or ZrO._{sub.2}.

23. A process of claim 20 where the concentration of the nanoscale metal oxide particles in the dispersion of step (a) is at least 20% by wt.

24. A process of claim 23 where the concentration of the nanoscale metal oxide particles in the dispersion of step (a) is at least 30% by wt.

27. A process of claim 20 where the plastic of the plastic substrate is a polyacrylate, polymethacrylate, polycarbonate, or polystyrene.

28. A plastic substrate provided with a nanostructured layer prepared by the process of claim 20.